

REMARKS/ARGUMENTS

Reconsideration is respectfully requested of the Official Action of July 13, 2007, relating to the above-identified application.

It is noted that the previous rejection of Claims 1 to 14 under 35 U.S.C. § 102(b) as being anticipated by *Hartmann, et al.*, U.S. 5,959,005 has been withdrawn. Also, it is noted that the rejection of Claims 1, 5, 6 and 15 to 17 under 35 U.S.C. § 102(b) in view of *Bock, et al.*, U.S. 6,020,419, has also been withdrawn.

With entry of the foregoing amendment, the claims in the case are 1, 3-6, 8, 9 11 and 13 to 17. It is noted that prosecution has been re-opened.

The rejection of Claims 1 to 14 as anticipated under 35 U.S.C. § 102(b) by *Michael, et al.*, published application U.S. 2002/0037936, is traversed and reconsideration is respectfully requested. The published U.S. application of *Michael* is assigned to the same assignee as the present application.

The *Michael* document describes the compacting of hydrophobic fumed silica using a roller compactor or preferably a belt filter press. See page 1, left-hand column, paragraph 0007.

The silicas of *Michael* have been rendered hydrophobic by using hexamethyldisilazane, trimethoxyoctylsilane or dimethylpolysiloxane; see paragraphs 0009-0012.

The claims in the present application require that the structurally modified pyrogenically produced silica contains the specific groups dimethylsilyl and/or monomethylsilyl on the surface of the silica, and further, that the silicas have a tamped density of 280 g/l or less. (See Claim 1). *Michael* does not describe the hydrophobization of a pyrogenic silica with dimethyl

dichlorosilane and/or monomethyl trichlorosilane in order to obtain dimethylsilyl groups or monomethylsilyl groups on the surface of the silica.

In addition, *Michael, et al.*, does not describe a silica that is ball milled to obtain a structurally modified pyrogenically produced silica.

The Office Action of July 13, 2007, has failed to point to any disclosure in the published application of *Michael, et al.*, that shows each and every limitation in Claim 1.

Consequently, *Michael* does not anticipate the subject matter of Claim 1 in this application.

It is also clear that *Michael* does not anticipate the subject matter of the process claims of this application such as Claim 3.

It should also be noted that the compacting of the silica following the techniques of *Michael* does not adversely affect the structure of the fumed silica because the tamped density is increased only. This is done by *Michael* in order to be able to pack more fumed silica into a single bag for shipping. The quality of the fumed silica has not been changed, only its density.

Applicants point out that the present invention accomplishes the structural modification of the fumed silica by milling with a ball mill. This feature has been emphasized in Claim 12. Attached hereto are two microphotos which show the structure for the aggregates of the fumed silica before the structural modification (top view) and after the structural modification (lower view). It can be seen in the lower figure that following the structural modification by ball milling, the aggregates of the fumed silica have been destroyed. This destruction of the silica structure is definitive and irreversible. The *Michael* patent fails to describe a destructured silica

having dimethylsilyl or monomethylsilyl groups on its surface. The destruction of the fumed silica is not inherent in the way in which *Michael* produces his fumed silica. There is no basis for the conclusion in the Office Action that these groups would inherently be present in the *Michael* silicas. Neither is there any basis to conclude that *Michael*'s silicas would possess the properties recited in Claim 1.

Accordingly, it is requested that the rejection on the grounds of anticipation under 35 U.S.C. § 102(b) be withdrawn.

The rejection of Claims 1 to 17 as allegedly obvious under 35 U.S.C. § 103(a) in view of *Bock, et al.*, U.S. 6,020,419, taken with *Nargiello, et al.*, U.S. 6,193,795, is traversed and reconsideration is respectfully requested. The *Bock* patent describes transparent coating compositions containing nano particles which enable the coatings produced from such liquid compositions to exhibit good scratch resistance. See column 2, lines 46 to 49. The invention in the *Bock* patent resides in the use of a jet dispersion technique to bring about a reduction in the agglomerate content of the pre-dispersion of nano particles containing agglomerates. The dispersions of the solids produced in that way are said to be useful as lacquer binders for transparent coatings. The patent points out that the dispersion of the nano particles produced by this jet dispersion method are resistant to re-agglomeration and settling in the presence of lacquer bindings. See column 2, beginning at line 50.

Bock, in column 3, beginning at line 57, explains that the pyrogenic silica nano particles can be used which have been surface treated with such materials as dimethyl dichlorosilane and/or monomethyl trichlorosilane.

In column 3, beginning at line 31, *Bock* explains that the nano particles in his transparent coating compositions are de-agglomerated by means of the dispersion process shown in U.S. patent 5,810,266 which shows production of finely divided dispersions using a jet mill.

In the examples of Table 1 of *Bock* in column 8, the coating compositions are also produced by the jet mill. Dispersions of surface modified fumed silica are dispersed in a polyacrylate with a hydroxyl content of 3%. See column 7, lines 42 to 57. These dispersions can be used immediately to lacquer coat aluminum sheets.

Although *Bock* uses the words "surface modified", the method of *Bock* is not identical to the structural modification according to the present invention because the structural modification of the present invention is done by a ball mill without any solvent or lacquer composition. Also, *Bock* does not describe the surface modification with dimethyl dichlorosilane or monomethyl trichlorosilane. *Bock* seeks to eliminate all agglomerates of the nano particles as he explains in column 2, line 50. This is necessary according to *Bock* in order to produce nano scale particles.

Thus, it can be seen that *Bock* is concerned with a production of lacquer coatings where it is necessary to produce nano particles which can be dispersed in a binder to form transparent coating compositions.

Suitable binders for use in the coating compositions of *Bock* are described beginning in column 4, at line 8.

In contrast, the *Nargiello* patent describes a method to modify the structure of fumed silica using a ball mill and is directed to producing fillers for polymers, sealants, caulking compounds and adhesives. See, for example, column 1, line 27 and 28. Also, the products of

Nargiello are used as fillers and carriers for non-polymer applications such as catalysts, refractories, ceramics and other purposes. See column 1, line 53 to 64. Nothing in *Nargiello* refers to the production of transparent lacquer coatings. A person skilled in the art searching for a suitable material for the lacquer coatings of *Bock* would not be led to select the destructured metal oxide filler of *Nargiello* for that purpose. Nothing in *Nargiello* would provide any motivation to a person skilled in the art that lacquer coatings of *Bock* could be improved by the addition of the *Nargiello* fillers or by the replacement of *Bock*'s nano particles. Consequently, applicants submit that the combination of references does not create *prima facie* obviousness.

It is particularly noteworthy that *Bock* has cited *Nargiello*. See column 1, lines 50 *et seq.* where *Bock* refers to the EP application, 637,616, (copy enclosed) which is equivalent to U.S. patent 6,193,795 of *Nargiello*. *Bock* says that the grinding as described by *Nargiello* may reduce agglomerates to one-sixth of their size; however, the low space/time yield and the unavoidable contamination due to the abrasion of the grinding additives are disadvantageous. Hence, *Bock* clearly points out that he would not utilize the *Nargiello* materials in his compositions. Consequently, it is readily apparent that a person skilled in the art such as *Bock* would not be motivated to rely on any of the teachings of *Nargiello* for incorporation of *Nargiello*'s fillers into the *Bock* compositions. Hence, applicants respectfully submit that the combination of *Bock* and *Nargiello* is clearly based on hindsight and, therefore, it is not a proper basis upon which to reject the claims.

The rejection of the claims under 35 U.S.C. § 103(a) should be withdrawn.

Favorable action at the Examiner's earliest convenience is respectfully requested.

Respectfully submitted,



By: Robert G. Weilacher, Reg. No. 20,531

Dated: November 8, 2007
SMITH, GAMBRELL & RUSSELL, LLP
Suite 3100, Promenade II
1230 Peachtree Street, N.E.
Atlanta, Georgia 30309-3592
Ph: (404) 815-3593
Fax: (404) 685-6893

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) Publication number:

0 637 616 A1

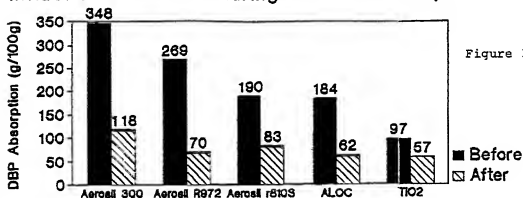
(12)

EUROPEAN PATENT APPLICATION(21) Application number: **94111862.2**(51) Int. Cl.⁸ **C09C 1/30, C09C 1/36,
C09C 1/40**(22) Date of filing: **29.07.94**(30) Priority: **02.08.93 US 100367
29.04.94 US 235699**(43) Date of publication of application:
08.02.95 Bulletin 95/06(64) Designated Contracting States:
BE DE FR GB(71) Applicant: **Degussa Aktiengesellschaft
Weissfrauenstrasse 9
D-60311 Frankfurt (DE)**

(72) Inventor: **Nargiello, Maria
1330 Weathervane Lane,
Apt. 2B
Akron, OH 44313 (US)**
Inventor: **Bush, Gary
4171 Seville Road
Seville, OH 44273 (US)**
Inventor: **Allen, Sturgis G.
1738 Northampton Road, No.904
Akron, OH 44333 (US)**

(64) **Low structure pyrogenic hydrophilic & hydrophobic metallic oxides, production and use.**

(67) A method of producing a low structure pyrogenic metal oxide filler is disclosed. The method involves subjecting pyrogenically produced metal oxide agglomerates and aggregates selected from silicon oxide, aluminum oxide, zirconium oxide, or titanium oxide to a dry milling process whereby the pyrogenically produced metal oxide is contacted in an agitating zone with an energy specific force.

Influence of Destructuring on DBP Absorption**EP 0 637 616 A1**

Background of the Invention

The present invention relates to low structure pyrogenic metal oxide fillers and to a method of producing such low structure pyrogenic metal oxide fillers. In a further aspect, the present invention also relates to products made from and containing the novel low structure pyrogenic metal oxide fillers.

Hydrophilic/hydrophobic pyrogenically produced metallic oxides based on silicon, aluminum, zirconium and titanium are well known in the art. They are produced by various methods known in the art such as described in U.S. Patent 3,954,945, U.S. Patent 4,067,954, and U.S. Patent 4,276,274 assigned to the assignee herein and all relied on and incorporated by reference in their entirety. Also known from the prior art is the fact that such oxides are used as reinforcing fillers in many silicone RTV/HTV/LTV and nonsilicone based polymeric formulations such as rubbery polymers, sealants, caulks and adhesives. A full description of silicone rubber chemistry is found in U.S. Patent No. 4,307,023 (which is incorporated by reference in its entirety, especially column 1, lines 5-30). The highest loadings possible are desired to obtain maximum reinforcement and improved physical properties including improved tensile strength, higher modulus, improved Shore A hardness and higher extrusion rates. Methods of producing hydrophobic pyrogenically obtained metallic oxide particulates are also well known in the art, as shown in U.S. Patent 4,068,024 and U.S. Patent 3,948,676 both assigned to the assignee herein.

The current problem when using pyrogenic metallic oxides is their high structure, measured by DBP Absorption, which prevents high filler loadings and causes excessive viscosity build-up and low extrusion rates which makes formulations difficult to handle and process. "Structure" as it relates to fillers is a well recognized and understood term, see Kirk Othmer Encyclopedia of Chemical Technology, volume 4, page 638.

Well known processes have been established to reduce particle/aggregate size and to decrease bulk density. However, simultaneously reducing particle size/aggregate size, decreasing bulk density and destructuring of pyrogenically produced metallic oxides is, prior to the present invention, an unknown process.

An object of the present invention is to provide low structure or destructured pyrogenic hydrophilic and hydrophobic metallic oxides which allow for higher loadings in formulations whereby excessive viscosity build-up is drastically reduced, extrusion rates are significantly increased, and mechanical properties are improved. Such low structure or destructured pyrogenic hydrophilic and hydrophobic metallic oxides can also be utilized as fillers and carriers for non-polymer applications such as catalysts, refractories, ceramics, and others. Mechanical destructuring is an irreversible process.

Summary of the Invention

Disclosed is a method of producing a low structure pyrogenic metal oxide filler; i.e., a pyrogenic metal oxide filler of reduced structure compared with the filler prior to being subjected to the method of the invention. The method involves subjecting pyrogenically produced metal oxide agglomerates and aggregates such as silicon oxide, aluminum oxide, zirconium oxide or titanium oxide to a dry milling process whereby the pyrogenically produced metal oxide is contacted in an agitating zone with an energy specific force created by certain reaction conditions.

The term "dry" as used herein means an extremely low moisture content. This is a condition known in the art as a "non-fluid medium" or a "non-fluid mill base". Since the pyrogenic methods of preparation of these metallic oxides do not involve an aqueous system, the products obtained are dry, and any moisture picked up would be adsorbed from the environment. In general, as used herein, the term "dry" means silicon dioxide having less than 2.5% moisture; aluminum oxide having less than 3% moisture; zirconium oxide having less than 1% moisture; and titanium oxide having less than 2% moisture.

The dry grinding process of the present invention is an intensive milling process which goes beyond standard particle size reduction to achieve destructuring of pyrogenic metallic oxides.

Agitating media bed used according to the invention are selected from stainless steel, chrome steel, carbon steel, ceramic, aluminum oxide, tungsten carbide, zirconium carbide, zirconium oxide, or zirconium silicate whereby the metallic oxide agglomerates and aggregates are free to move, collide and impinge between the colliding media. The media is kept in constant agitation by a rotating shaft with protruding extensions of a desired length or by a rolling drum. The media diameter is generally one quarter inch to one inch in diameter and being of circular, spherical or cylindrical shape (or equivalents thereof). The shaft speed is between 100 and 1500 rpm or the roller drum speed is between 30 to 120 rpm. It is a feature of the invention that the media fills the volume of the agitating zone to the extent of 1/4 to 3/4 of the total volume and wherein the dwell time in the zone is controlled by the amount of time the metallic oxide

remains in the media bed or by the number of passes through the media bed. The product stream is evaluated to ascertain the structure of the resulting product until a steady state condition is reached. The lowering of the structure of the pyrogenic metallic oxide is a function of the time of compression, the amount of compressive force exerted on the aggregate/agglomerate particles and the conditions of compression.

Brief Description of the Drawings

The invention will be further understood with reference to the drawings, wherein:

Figure 1 is a bar chart showing the influence of destructuring on DBP absorption;
Figure 2 is a bar chart showing the influence of destructuring on agglomerate size; and
Figure 3 is a bar chart showing the influence of destructuring on bulk density.

Detailed Description of the Invention

According to the present invention, reduced particle/aggregate size, extremely reduced bulk density and destructured products are manufactured by taking hydrophilic/hydrophobic pyrogenic metallic oxides and passing them through a dry milling process whereby the products come into contact with an energy specific force created by the following conditions:

- Agitating media (specific density 2.3-8 g/cm³, examples include stainless or chrome or carbon steel, ceramic, tungsten or zirconium carbide, zirconium oxide or zirconium silicate) so that the metallic oxide agglomerates/aggregates are free to move, collide and impinge upon each other.
- Media is kept in constant agitation by a stationary shaft (vertical or horizontal) with protruding extensions of a length determined by the size of the vessel or by a rolling drum.
- The media diameter is 0.04 - 1 inch in diameter.
- The media can be either spherical, cylindrical or other shapes used in the art.
- The shaft speed must be between 100-1500 rpm or the rpm of the rolling drum must be between 30-120 rpm.
- At rest, the media used must fill 1/4 - 3/4 of the volume of the chamber or vessel used for destructuring.

The stationary rotating shaft refers to a shaft whose only motion is its rotation along its axis. The protruding extensions of the stationary shaft are of varying lengths which achieve fluidization of the media.

Time is very important in the process of the present invention because destructuring takes place after a critical reduced particle/aggregate size and bulk density have been achieved. The dwell time where the pyrogenic metallic oxide is in contact with the agitating media is controlled by either:

1. the amount of time the metallic oxide remains in the media bed or
2. by the number of passes through the media bed.

Examples of these mills include ball mills, attrition mills, and others known in the art. Destructuring is also accomplished by intense compression through a roller mechanism, whereby, for example, the silica is compressed upon itself, between roller devices or between roller devices and a stationary vessel wall. An example of these types is a roller mill (i.e., 2-roll mill or 3-roll mill) and others known in the art.

A correctly operating mill such as a ball mill is characterized by a typical movement traveled by a typical ball in a partially filled ball mill chamber. Low velocity of the ball mill causes the typical ball inside the mill to be gradually lifted up on one side of the mill to a higher and higher level. At that point the ball cascades, falling and tumbling down along the sloping surface to the low side of the mill. Three types of movements are recognized in connection with operating ball mills; namely, centrifuging, cataracting and cascading. These characteristic actions in a ball mill are known and recognized in the art. The desirable movement is cascading and persons skilled in the art recognize what is meant by this term. Cascading is a highly efficient process for producing a finely divided material and is the goal of the successful operation of the invention.

Charging the ball mill or attrition mill to a partial capacity, such as halfway, provides the most efficient loading arrangement. Optimum loading complies with theoretical considerations and cascading freely occurs throughout the mill.

Ceramic ball media, such as flint pebbles and porcelain balls, were historically supplied in a range of sizes as indicated above. Steel balls and other newer technology types as known in the art are commonly supplied in ball diameters which also can vary, but in accordance with the present invention it has been found that dimensions of 0.04 inch to 1 inch diameter are preferable. The approximate number of balls, n, per pound can be calculated from the expression $n = 53/pd^2$, wherein p is the ball density given in grams

per cubic centimeter and d is the ball diameter in inches. Thus, the number of porcelain balls of a certain size and density can be calculated per pound.

Ball mills are normally equipped with a manhole for loading the charge from the top which can be facilitated by a slope shoot that reaches from the storage area to the surface of the ball mill charge inside the mill, an air relief valve and a venting port for discharge. Venting should be carried out after starting a new batch and periodically as necessary as it contributes to grinding efficiency. Since the flowing material or moving machinery generates static electricity, it is desirable to have grounding at all points.

Although naturally occurring ceramic media such as flint pebbles (low density) are the oldest grinding material that is known, it is preferable to use the newer high density porcelain balls which have a high density. These are well known materials which are harder and more abrasion resistant than more conventional older porcelains and hence the wear on the ball is correspondingly less.

Metallic media are generally of a higher density than porcelain balls and therefore provide faster grinding at smaller ball diameters than their ceramic counterparts. This usually necessitates sturdier mill construction and higher power requirements. High carbon, high manganese steel balls having a Rockwell C hardness of 60 to 70 are commonly used for ball mill operations.

In selecting ball size, the smallest size should be selected which provides the proper cascading action inside the mill. It has been determined that once the ball size has been established for providing the best grinding action, it does not vary appreciably for different size mills. Thus, the ball size that proves successful on a small ball mill usually is also suitable to a scaled up production system. In general, balls of a minimum diameter and a maximum density are necessary to achieve the proper cascading action should be selected because per revolution of the mill they provide the maximum number of impact, colliding, or shearing contacts and for a given volume of space offer the maximum area for compressive action. Also, the smaller void spaces between the balls of lesser diameter effectively limits the size of the mill base agglomerates that can exist in the interstitial space.

It will be seen that depending upon the ball diameter and density, the most favorable conditions for grinding in a ball mill are tied in closely with the density and velocity of the mill base. In the difference between the ball and the mill base density, Δp determines the actual force acting on the balls that causes them to cascade. The buoyant effect exerted by the mill base acting upwardly is proportional to the mill base density. The gravitational pull or weight of the ball charge acts downwardly and is proportional to the ball density. Hence it has been said that the overall or net force acting downward is proportional to the difference in the two densities and is given in the following equation: $\Delta p = p(\text{ball}) - p(\text{mill base})$

While it has been suggested by some to use a mixture of small and large ball sizes in a ball mill operation, it has been found herein that it is desirable if the balls are of similar size.

When the charge is added to the ball mill ready for grinding, the metallic oxide proceeds to fill into the voids between the balls.

Taking into consideration that depending upon the ball shape and size, there can be a relatively tight packing of the balls or a relatively loose packing of the grinding medium. On an average, for a ideal situation assuming ideal charging conditions, the empty space in the ball mill should be about 50%, the ball volume occupying 30% of the remainder and the metallic oxides the remaining 20%. These are approximate and are not narrowly critical. It was established in general that by charging the ball mill to the halfway mark with balls, maximum grinding efficiency is obtained although that can vary as explained above.

If an amount of the metallic oxide is used that is greater than necessary to cover the balls in the ball mills (overpacking the chamber), the excess remains undischarged with respect to the balls until such time as it has the opportunity to defuse into and displace some of the metallic base that is in the active ball region. This means that the operation is not being carried out under optimum conditions.

The difference between a ball mill vibrating in a horizontal mode and an attrition mill is well known. Whereas conventional ball milling is based on the cascading of the ball media in a horizontally mounted rotating drum, the attrition mills generally are upright, stationary, cylindrical grinding tanks fitted with a centralized vertical rotating shaft to which is attached at right angles a distribution of agitation members or metallic fingers. These extensions protrude into the ball media mill base mixture which partially fills the attritor tank during the milling operation. The rotation of these fingers which sweep through the tank contents vigorously agitates the ball charge which in turn provides the necessary shear and impact forces to grind the metallic oxide. The attritor mills can be designed for either batch or continuous operation. When properly functioning, the attritor mill also keeps all of the ball media in constant motion due to the rotation of the agitator fingers on the central shaft. Thus, in actual rotation the grinding media fluidizes and occupies a far greater percentage of the volume of the agitator than when the rotating blade is at rest. It is therefore essential that in a ball mill cascading action is obtained whereas in the attritor mill fluidization of the balls and agitating medium is necessary.

It is possible to use milling procedures which compact the metallic oxide which decrease the bulk density without destructuring (see Tables 1 and 2).

In all cases, lowering the structure of pyrogenic metallic oxides is a function of:

1. the time of compression
2. the amount of compressive force exerted on the aggregates/agglomerate particles
3. the conditions of compression.

Destructuring takes place when these three facets of compression have been optimized. The destructuring process can be either continuous or batch. In all cases, destructuring is irreversible. Destructuring according to the present invention is achieved in a dry grinding process. As opposed to a wet grinding process, dry grinding is a more intense milling process which goes beyond standard particle size reduction to achieve destructuring of pyrogenic metallic oxides. Prior to the present invention, destructuring of pyrogenic metallic oxides has not been documented. In wet grinding, particles are surrounded by liquid (e.g., water or resin). Particle size is reduced with the milling energy generated by wet grinding; however, structure is much less influenced since the liquid acts like a cushion, thus metallic oxides can not be destructured effectively by wet grinding.

In addition to reducing the DBP absorption, the destructuring process of the present invention reduces agglomerate size measured by differential number % by Coulter® Laser Particle Size Analysis using optical model of Fraunhofer and bulk density measured in g/l. In general, destructuring according to the present invention achieves a 40% to 90% lowering of structure.

The present invention pertains to destructuring of all pyrogenic hydrophilic/hydrophobic metallic oxides with the following physical-chemical properties:

1. Pyrogenic Silicon Dioxide (hydrophilic & hydrophobic):

BET -Surface Area m ² /g (Micromeritics® 2300)	50 - 400
Average Particle Size nm	7 - 40
Bulk Density g/l (DIN 53194)	20 - 120
Loss of Drying % (DIN 55921)	0.5 - 2
Loss of Ignition % (DIN 55921)	1 - 10
pH (DIN 53200)	3 - 9
DBP Absorption g/100g (DIN 53601)	150 - 450
Carbon Content %	0 - 5

Hydrophobizing agents for pyrogenic silicon dioxide include silane/organosilicon compounds (e.g., silicone oil, dimethyldichloro silane, hexamethyldisilazane, and others known to those skilled in the art) which consist of linear or cyclic organopolysiloxanes. The free valences of silicon not bonded to oxygen can be taken up by organic groups or hydrogen. For details of the hydrophobizing agents refer to U.S. Patent No. 4,307,023 (which is incorporated by reference in its entirety, especially column 2, lines 5-30). Further details of the hydrophobizing process can be found in U.S. Patent Nos. 3,924,029 and 4,503,092 (which are incorporated by reference in their entirety). U.S. Patent 4,326,852 is also incorporated by reference in its entirety. The referenced patents illustrate hydrophobizing agents and methods for treating silica to render it hydrophobic.

2. Pyrogenic Aluminum Oxide:

BET -Surface Area m ² /g (Micromeritics® 2300)	80 - 120
Average Particle Size nm	10 - 15
Bulk Density g/l (DIN 53194)	40 - 120
Loss of Drying % (DIN 55921)	1 - 5
Loss of Ignition % (DIN 55921)	1 - 3
pH (DIN 53200)	4.5 - 5.5
DBP Absorption g/100g (DIN 53601)	150 - 200

3. Pyrogenic cofumed mixed metallic oxides of above silicon dioxide products and aluminum oxide in ratios of 1 - 5% Al₂O₃:SiO₂.

4. Physical blends of pyrogenic metallic oxides of the above silicon dioxide products and aluminum oxide in ratios up to 20% Al₂O₃:SiO₂.

5. Pyrogenic Titanium dioxide:

BET -Surface Area m ² /g (Micromeritics® 2300)	30 - 100
Average Particle Size nm	15 - 30
Bulk Density g/l (DIN 53194)	40 - 120
Loss of Drying % (DIN 55921)	1 - 2
Loss of Ignition % (DIN 55921)	1 - 2
pH (DIN 53200)	3.0 - 4.0
DBP Absorption g/100g (DIN 53601)	90 - 130

6. Pyrogenic Zirconium Oxide:

BET -Surface Area m ² /g (Micromeritics® 2300)	30 - 50
Average Particle Size nm	20 - 40
Bulk Density g/l (DIN 53194)	80 - 250
Loss of Drying % (DIN 55921)	.1 - 1
Loss of Ignition % (DIN 55921)	.1 - 1
pH (DIN 53200)	5.5 - 6.5
DBP Absorption g/100g (DIN 53601)	120 - 150

Step 1. Production of Destructured Products

Trials were conducted with one pyrogenic hydrophilic silicon dioxide (Aerosil® 300), two hydrophobic pyrogenic silicon dioxide products (Aerosil® R972 & R810S), one pyrogenic aluminum oxide (Aluminum Oxide C), and one pyrogenic titanium dioxide (Titanium dioxide P-25). Aerosil® is a trademark of Degussa AG for its brand of pyrogenic silica. These are commercially available products with well documented properties and characteristics. 1000 grams of pyrogenic metallic oxide were charged (via a continuous gravity feed or one single charge) into an agitating media bed with a retention time of 15 seconds to 10 minutes for attrition process and 1-4 hours for batch roller mill process. After the destructuring procedure, the physical-chemical characteristics are as follows:

	DBP Absorption (g/100g)	Agglomerate Size (μ)	Bulk Density (g/l)
Aerosil® 300			
Before destructuring	348	12.0	25
After destructuring	118	2.0	308
Aerosil® R972			
Before destructuring	269	9.0	30
After destructuring	70	5.0	308
Aerosil® R810S			
Before destructuring	190	13.0	30
After destructuring	83	4.0	270
Al₂O₃C			
Before destructuring	184	2.7	45
After destructuring	62	0.3	614
TiO₂P-25			
Before destructuring	97	0.6	117
After destructuring	57	0.2	525

The above data shows that the destructuring obtained was approximately 40% to 90%.

Destructuring is time/force related. Optimized conditions were defined as volume of ball mill-one gallon, charge of Aerosil 200VS-250 grams, charge of ceramic media (1/4 inch spherical, density 2.8 g/cm³)-5000

grams, rpm of ball mill-90 rpm; samples were taken over several periods of time and the following destructuring under optimized conditions are achieved:

Table 1

Aerosil 200 VS	DBP absorption g/100g
no milling	290
1 hour	213
2 hours	174
3 hours	149
4 hours	136

Examples where mechanical compaction does not destructure but where bulk density is reduced are evident by comparing standard undensified grades of silica produced by Degussa AG, Aerosil® 200, 200m²/g and Aerosil® 300, 300m²/g to their densified counter parts:

Table 2

		Bulk Density g/l	DBP g/100g
Aerosil®	200	20	309
	200VS	85	290
Aerosil®	300	25	360
	300VS	90	350

For densification process, see U.S. Patent Nos. 2,112,949; 2,844,459; and 4,877,595 (which are incorporated by reference in their entirety).

Non-optimized ball milling conditions, which do not significantly influence structure, are defined as volume of ball mill-one gallon, charge of Aerosil® 200-150 grams, charge of ceramic media (1/4 inch spherical, density 2.8 g/cm³)-varied as indicated below, rpm of ball mill-90 rpm, time-varied as indicated below:

Treatment	DBP g/100 g
no treatment (as is)	321
250 g of media, milled 5 minutes	324
350 g of media, milled 15 minutes	310
650 g of media, milled 15 minutes	307
1000 g of media, milled 15 minutes	296

Step 2. Use of destructured products to improve extrusion rate (ASTM C603)

Preblend 36 g of crosslinker {vinyl-tris(methylethyl-ketoxime) silane} with 300 g of polydimethylsiloxane - silanol terminated resin (20,000 centistoke). Then add 30 g of pyrogenic metallic oxide into 336 g of resin + crosslinker. (This mixture is part A).

Mix part A 20 minutes using high speed dispersion. While mixing part A, preblend dibutyl-tin dilaurate based catalyst with 1000 centistoke polydimethylsiloxane fluid. (This is part B.) Mix part B for 5 minutes under high speed dispersion. Then mix part A and B 5 minutes under high speed dispersion. Afterwards, mix additional 20 minutes under low speed. After dispersion, fill Semco® tubes and test extrusion rate according to ASTM C603. Extrusion rates of structured and destructured materials are as follows:

	Extrusion Rate (g/min.)
Aerosil® 300	
Before destructureuring	306
After destructureuring	578
Aerosil® R972	
Before destructureuring	490
After destructureuring	888
Aerosil® R810S	
Before destructureuring	526
After destructureuring	834

Low structure is important to be able to load the polymer with larger amounts of filler. It enhances reinforcement and good flow properties of the polymer.

Step 3. Use of destructured Products to reduce viscosity measured by Brookfield®

Blend 10 parts pyrogenic metallic oxide (e.g., silica) with 100 parts 8000 centistoke polydimethylsiloxane resin. Mix with high speed dispersion for 10 minutes. Allow to sit for 4 hours and measure viscosity with RVT Brookfield® viscometer with T-spindle at 20 rpm.

	Viscosity (cps)
Aerosil® 300	
Before destructureuring	10,000,000
After destructureuring	17,500
Aerosil® R972	
Before destructureuring	60,000
After destructureuring	25,000
Aerosil® R810S	
Before destructureuring	30,000
After destructureuring	26,000

Step 4. Hydrophobizing in-situ or as an after-treatment.

During the destructureuring process hydrophobized surfaces open up, exposing untreated internal surfaces. To fully hydrophobize these surfaces it is necessary to rehydrophobize during the destructureuring process or an after-treatment once destructureuring is completed. Any silane/siloxane treatments cited above for hydrophobizing of pyrogenic silicon dioxide can be utilized here.

Further variations and modifications of the foregoing will be apparent to those skilled in the art and such variations and modifications are attended to be encompassed by the claims that are appended hereto.

Claims

1. A method of producing a low structure pyrogenic metal oxide filler comprising, subjecting pyrogenically produced metal oxide agglomerates and aggregates selected from the group consisting of silicon dioxide, aluminum oxide, and titanium oxide to a dry milling process whereby the pyrogenically produced metal oxide is contacted in a agitating zone with an energy specific force created by the following conditions:

agitating media bed consisting of a member selected from the group consisting of stainless steel, chrome steel, carbon steel, ceramic, aluminum oxide, tungsten carbide, zirconium carbide, zirconium

oxide, and zirconium silicate whereby the metallic oxide agglomerates and aggregates are free to move, collide and impinge on each other, wherein the media is kept in constant agitation by a rotating shaft with protruding extensions of a length or by a rolling drum, the media diameter being 0.04 to one inch in diameter and being of circular, spherical or cylindrical shape, the shaft speed being between 100 and 1500 rpm or the roller drum speed being between 30 to 120 rpm, wherein the media fills the volume of the agitating zone to the extent of 1/4 to 3/4 of its total volume and wherein the dwell time in the zone is controlled by the amount of time the metallic oxide remains in the media bed or by the number of passes through the media bed, evaluating the resulting product until a steady state condition is reached and wherein the lowering of the structure of the pyrogenic metallic oxide is a function of the time of compression, the amount of compressive force exerted on the aggregate/agglomerate particles and the conditions of compression.

2. The method according to claim 1 wherein the metallic oxide is pyrogenic silicon dioxide having the following characteristics:

BET -Surface Area m ² /g	50 - 400
Average Particle Size nm	7 - 40
Bulk Density g/l (DIN 53194)	20 - 120
Loss of Drying % (DIN 55921)	0.5 - 2
Loss of Ignition % (DIN 55921)	1 - 10
pH (DIN 53200)	3 - 9
DBP Absorption g/100g (DIN 53601)	150 - 450
Carbon Content %	0 - 5

3. The method according to claim 1 wherein the metallic oxide is pyrogenic aluminum oxide having the following characteristics:

BET -Surface Area m ² /g	80 - 120
Average Particle Size nm	10 - 15
Bulk Density g/l (DIN 53194)	40 - 120
Loss of Drying % (DIN 55921)	1 - 5
Loss of Ignition % (DIN 55921)	1 - 3
pH (DIN 53200)	4.5 - 5.5
DBP Absorption g/100g (DIN 53601)	150 - 200

4. The method according to claim 1 wherein the metallic oxide is a pyrogenic cofumed mixed metallic oxide of silicon dioxide and aluminum oxide in a ratio of 1 - 5% Al₂O₃:SiO₂.

5. The method according to claim 1 wherein the metallic oxide is a physical blend of pyrogenic metallic oxides of silicon dioxide and aluminum oxide in a ratio up to 20% Al₂O₃:SiO₂.

6. The method according to claim 1 wherein the metallic oxide is pyrogenic titanium oxide having the following characteristics:

BET -Surface Area m ² /g	30 - 100
Average Particle Size nm	15 - 30
Bulk Density g/l (DIN 53194)	40 - 120
Loss of Drying % (DIN 55921)	1 - 2
Loss of Ignition % (DIN 55921)	1 - 2
pH (DIN 53200)	3.0 - 4.0
DBP Absorption g/100g (DIN 53601)	90 - 130

7. The method according to claim 1 wherein the metallic oxide is pyrogenic zirconium oxide having the following characteristics:

BET -Surface Area m ² /g	30 - 50
Average Particle Size nm	20 - 40
Bulk Density g/l (DIN 53194)	80 - 250
Loss of Drying % (DIN 55921)	.1 - 1
Loss of Ignition % (DIN 55921)	.1 - 1
pH (DIN 53200)	5.5 - 6.5
DBP Absorption g/100g (DIN 53601)	120 - 150

8. A method of using the low structure pyrogenic metallic oxide according to claim 1 comprising incorporating a sufficient amount of said metallic oxide to function as a reinforcing filler in a silicon or non-silicon based rubber, sealant, caulk or adhesive composition.
9. A low structure pyrogenic metal oxide filler or carrier produced by the method according to claim 1.
10. A polymeric composition comprising a silicone or non-silicone based polymeric containing as a reinforcing filler a sufficient amount of the filler produced according to the method of claim 1.
11. The polymeric composition according to claim 10 which is a rubber, sealant, caulk or adhesive composition.
12. A rubber composition comprising a silicone or non-silicone based rubber containing as a reinforcing filler a sufficient amount of the filler produced according to the method of claim 1.
13. A sealant composition comprising a silicone or non-silicone based sealant containing as a reinforcing filler a sufficient amount of the filler produced according to the method of claim 1.
14. A caulk composition comprising a silicone or non-silicone based caulk containing as a reinforcing filler a sufficient amount of the filler produced according to the method of claim 1.
15. An adhesive composition comprising a silicone or non-silicone based adhesive containing as a reinforcing filler a sufficient amount of the filler produced according to the method of claim 1.
16. A method of producing a low structure pyrogenic metal oxide filler, said method consisting essentially of subjecting pyrogenically produced metal oxide agglomerates and aggregates selected from the group consisting of silicon dioxide, aluminum oxide, and titanium oxide to a dry milling process whereby the pyrogenically produced metal oxide is contacted in a agitating zone with an energy specific force created by the following conditions:
- agitating media bed consisting of a member selected from the group consisting of stainless steel, chrome steel, carbon steel, ceramic, aluminum oxide, tungsten carbide, zirconium carbide, zirconium oxide, and zirconium silicate whereby the metallic oxide agglomerates and aggregates are free to move, collide and impinge on each other, wherein the media is kept in constant agitation by a rotating shaft with protruding extensions of a length or by a rolling drum, the media diameter being 0.04 to one inch in diameter and being of circular, spherical or cylindrical shape, the shaft speed being between 100 and 1500 rpm or the roller drum speed being between 30 to 120 rpm, wherein the media fills the volume of the agitating zone to the extent of 1/4 to 3/4 of its total volume and wherein the dwell time in the zone is controlled by the amount of time the metallic oxide remains in the media bed or by the number of passes through the media bed, evaluating the resulting product until a steady state condition is reached and wherein the lowering of the structure of the pyrogenic metallic oxide is a function of the time of compression, the amount of compressive force exerted on the aggregate/agglomerate particles and the conditions of compression.

Influence of Destructuring on DBP Absorption

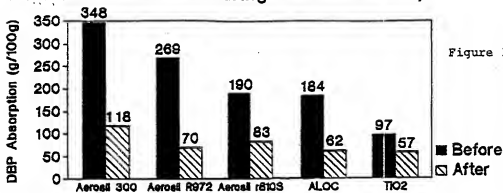


Figure 1

Influence of Destructuring on Agglomerate Size

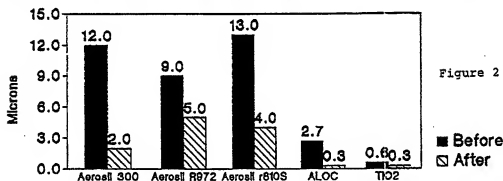


Figure 2

Influence of Destructuring on Bulk Density

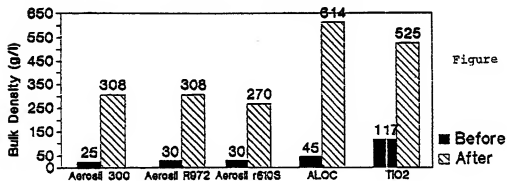


Figure 3



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 94 11 1862

DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
A	EP-A-0 469 257 (VAM ALUMINIUM AG) * claim 2 * ---	1,3
A	US-A-4 722 952 (BRIAN W. HATT) * claim 1 * ---	1,2
A	EP-A-0 492 238 (BAYER AG) * claim 1 * ---	1
A	FR-A-2 415 128 (BASF FARBEN & FASERN) * claim 1 * ---	1,6
A	DE-A-29 44 791 (TIOXIDE GROUP LTD) * claim 1 * ---	1,6
A	DE-A-27 21 294 (NATIONAL SEMICONDUCTOR CORP) * page 4, line 1 - page 6, line 7 * -----	1,2
The present search report has been drawn up for all claims		
Place of search BERLIN		Date of completion of the search 4 October 1994
Examiner Clement, J-P		
CATEGORY OF CITED DOCUMENTS		
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		
T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons A : member of the same patent family, corresponding document		

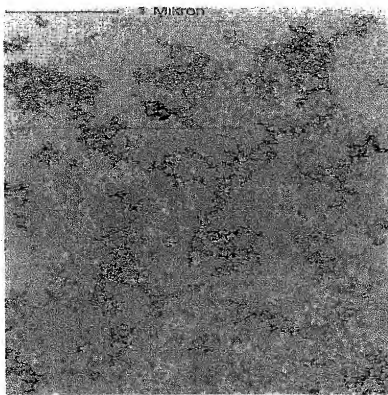
CLASSIFICATION OF THE
APPLICATION (Int.Cl.6)

C09C1/30
C09C1/36
C09C1/40

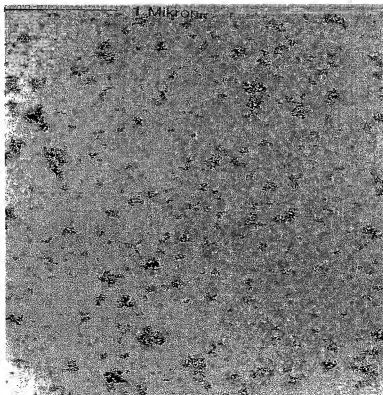
TECHNICAL FIELDS
SEARCHED (Int.Cl.6)

C09C

The Effect Of Structural Modification Of Pyrogenic Oxides As Shown In
TEM Photos.



Not Structurally Modified



Structurally Modified